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A Proton-Triggered Cascade Reaction Involving a Heavy p-Block Multiple Bond: Transformation of the Diphosphene $C_5Me_5P{=}PC_5Me_5$ into the Cationic Cage $[C_{10}Me_{10}P_2H]^+$

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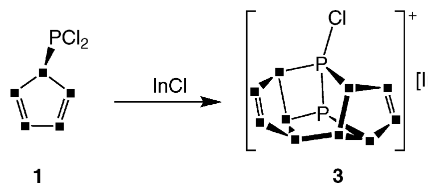
Protonation of one of the phosphorus centers of the diphosphene $C_5Me_5P{=}PC_5Me_5$ triggers a remarkable cascade reaction leading to the direct formation of a $C_{10}P_2$ cage. Calculations suggest that the key mechanistic feature is the proximity of a C=C π-system to a developing positive charge on one of the phosphorus centers.

Yoshifuji and Inamoto's seminal report of the synthesis and isolation of the diphosphene mes*P=Pmes* (**A**, mes* = 2,4,6-tri-*tert*-butylphenyl)[1] exploded the myth that such bonds could not exist under ambient conditions. Much effort over the past quarter of a century has aimed to explore the reactivity of this unusual class of compound, but the simple classification of reactivity in the way that has been achieved in organic chemistry has been hampered by the lack of mechanistic insight. Our own interest in this topic derived from our recent report[2] that the addition of the low oxidation state group 13 halides InCl or "GaI" to $C_5Me_5PCl_2$ (**1**) results (Scheme 1) in the quantitative and stereoselective formation of the diphosphorus cages $[C_{10}Me_{10}P_2X]^+[MX_nCl_{4-n}]^-$ (**2**, M = Ga, X = I, n = 0–4; **3**, M = In, X = Cl). We were intrigued by the fact that the cores of **2** and **3** are isomeric with the well-known diphosphene $C_5Me_5P{=}PC_5Me_5$ (**4**),[3,4] although the nature of the bonding in the two cases is clearly completely different. The $(CR)_{10}P_2$ unit is also isolobal with the hydrocarbon $C_{12}H_{12}$, the isomers of which have been the subject of numerous studies, both experimental and theoretical.[5]

The cage species **2** and **3** can be viewed, at least formally, as adducts of a neutral $C_{10}P_2$ unit with a Cl^+ ion, and this led us to wonder whether it might be possible to access the isolated cage by triggering a cascade reaction[6] through protonation of the P=P double bond in **4**. In this respect we were encouraged by the previous reports that Inamoto's mesityl diphosphene, **A**, reacts with HBF_4 to form a phosphacycle[7,8] and is also methylated by $MeOSO_2CF_3$,[9] although strongly forcing conditions in the form of a 35-fold excess of the methylating reagent are required to drive this.



Scheme 1. ■ = CMe.

Reaction of a bright yellow CH_2Cl_2 solution of **4** with an equimolar amount of triflic acid (CF_3SO_3H) at 0 °C results in a yellow/brown solution of **5**. The reaction is quantitative and essentially instantaneous even when the temperature is reduced to –78 °C. The ^{31}P NMR spectrum of the reaction mixture showed two resonances resulting from an HP–P unit [δ = 24.0 (dd, $^1J_{PP}$ = 179, $^1J_{PH}$ = 425 Hz), 14.6 (dd, $^1J_{PP}$ = 179, $^2J_{PH}$ 15 Hz) ppm],[10] both of which are shifted considerably upfield from that of **4** (singlet at δ = 504.0 ppm). The ^{31}P NMR spectrum of the resulting product is also wholly different from that of the methylation product of **A**[1] reported by Grützmacher et al.[9] [δ = 237.0 (d), 332.2 (d) ppm, $^1J_{PP}$ = 633 Hz],[9] and from that of the phosphacycle synthesised by Cowley et al.[7,8] by protonation of **A**. The ^{31}P and ^1H NMR spectra were, however, highly reminiscent of the corresponding spectra of **2** and **3** [for **2**: δ = 68.7 (d), 29.0 (d) ppm, $^1J_{PP}$ = 231 Hz; for **3**: δ = 126.5 (d), 24.7 (d) ppm, $^1J_{PP}$ = 246 Hz; both show ten separate signals for methyl groups in their respective ^1H NMR spectra].[2] This led us to speculate that the product **5** might be $[C_{10}Me_{10}P_2H]^+[OSO_2CF_3]^-$ (Scheme 2) containing a $C_{10}P_2$ cage similar to that found[2] in **2** and **3**. Initial attempts to obtain crystals of **5** suitable for an X-ray crys-

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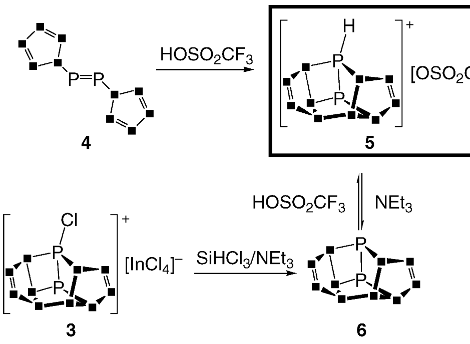
tallographic study were unsuccessful, but the relationship between **3** and **5** was confirmed by reduction {P^V/P^{III}} of **3** using $HSiCl_3$ and Et_3N,[11] which afforded a quantitative yield of the neutral cage compound $C_{10}Me_{10}P_2$ (**6**). Subsequent protonation of **6** with triflic acid (0 °C, CH_2Cl_2) led to the selective formation of **5** in analytically quantitative yield; this reaction is reversible as treatment of **5** with NEt_3 leads to the quantitative reformation of **6**.



Scheme 2. ■ = CMe.

The neutral cage compound **6**, which is air- and moisture-stable, was characterised by EI mass spectrometry which gave a molecular ion peak at 332 amu and by ^{31}P NMR spectroscopy which showed two doublets characteristic of the P–P bonded cage (δ = 15.9, –13.3 ppm, $^1J_{PP}$ = 148 Hz). Unequivocal confirmation of the structure was provided by a single-crystal X-ray diffraction experiment (see Figure 1). Complex **6** crystallises in the centrosymmetric space group *P*2(1)/*n*, and the diffraction data, although of modest quality, clearly showed the core structure of **6** to be closely related to the cationic cages of **2** and **3**, with the only notable differences being that the P–P and P–C bond lengths to the phosphorus atom of the P–X unit in **2** and **3** are somewhat shorter than the analogous bonds in **6** as a result of the formal positive charge at phosphorus atoms in the cationic cages.[2]

Thus, the experimental data suggests that protonation of the diphosphene **4**, which is isolobal with an alkene, leads to a cascade reaction and the selective formation of the cage compound **5**. Although cascade reactions have played, and will undoubtedly continue to play, an important role in natural product syntheses, the reaction **4** → **5** (Scheme 2) represents a new type of process where a homonuclear heavy p-block multiple bond is an integral component of the process, allowing the construction, in *one* synthetic operation, of the $C_{10}P_2$ cage structure present in **5**; this provides an interesting contrast with the multistep syntheses of the corresponding hydrocarbon systems.[12] Within the wider context of cascade reactions in inorganic chemistry, we note the report by Driess and co-workers of the formation of a phosphonium cage through methylation of a phosphanylidene.[13]

The overall reaction **4** → **5** involves the formation of three strong bonds (two P–C and one C–C), steps that are usually associated with a significant activation barrier. The fact that the reaction is instantaneous at –78 °C, with no observable intermediates, prompted us to use density functional theory to explore available pathways for the cascade reaction leading to **5**. For computational expedience we have replaced the methyl groups with hydrogen atoms, and these model compounds are labelled with a prime (′) to distinguish them from the methylated compounds labelled **3**–**6**.

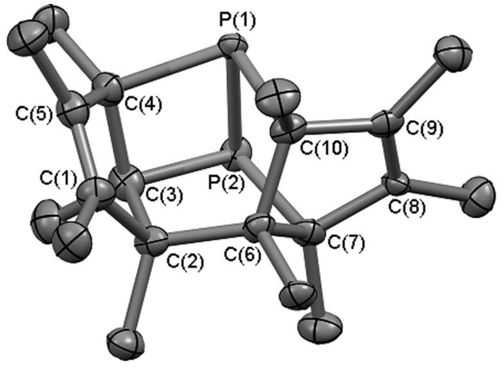


Figure 1. Molecular structure of **6**. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°]: P(1)–P(2) 2.230(2), P(1)–C(10) 1.888(6), P(1)–C(4) 1.896(7), P(2)–C(7) 1.905(6), P(2)–C(3) 1.933(7), C(7)–C(8) 1.512(9), C(7)–C(6) 1.544(9), C(5)–C(1) 1.532(9), C(5)–C(4) 1.584(9), C(5)–C(6) 1.596(9), C(9)–C(8) 1.336(9), C(9)–C(10) 1.504(9), C(6)–C(10) 1.561(9), C(3)–C(2) 1.489(9), C(3)–C(4) 1.527(10), C(1)–C(2) 1.323(10); C(10)–P(1)–C(4) 93.6(3), C(10)–P(1)–P(2) 92.6(2), C(4)–P(1)–P(2) 78.1(2), C(7)–P(2)–C(3) 101.9(3), C(7)–P(2)–P(1) 89.9(2), C(3)–P(2)–P(1) 77.4(2), C(8)–C(7)–C(6) 103.5(5), C(8)–C(7)–P(2) 99.1(4), C(71)–C(7)–P(2) 112.0(5), C(6)–C(7)–P(2) 108.5(4), C(1)–C(5)–C(4) 101.5(5), C(1)–C(5)–C(6) 110.9(5), C(4)–C(5)–C(6) 106.3(5), C(8)–C(9)–C(10) 109.1(6), C(7)–C(6)–C(10) 97.2(5), C(7)–C(6)–C(5) 115.8(5), C(10)–C(6)–C(5) 108.2(5), C(9)–C(10)–C(6) 103.6(5), C(9)–C(10)–P(1) 106.0(4), C(6)–C(10)–P(1) 101.9(4), C(9)–C(8)–C(81) 127.8(6), C(9)–C(8)–C(7) 109.4(6), C(2)–C(3)–C(4) 105.3(5), C(2)–C(3)–P(2) 112.3(5), C(4)–C(3)–P(2) 97.3(4), C(3)–C(4)–C(5) 101.1(5), C(3)–C(4)–P(1) 99.0(4), C(5)–C(4)–P(1) 108.4(4), C(2)–C(1)–C(5) 111.2(6), C(1)–C(2)–C(3) 110.6(6).

A potential energy surface for the reaction is summarised in Figure 2, along with the optimized structures of the various stationary points. The optimised structure of the cage compound **6′** is in excellent agreement with experiment, with a P–P bond length of 2.28 Å compared to 2.230(2) Å in the X-ray structure. Test calculations using the fully methylated species **6**, confirm that, although the methyl groups increase the steric crowding to some extent, they have no significant impact on the bond lengths of the cage itself. Protonation of **6′** at P(1) to form **5′** causes a contraction of the P–P σ-bond from 2.28 Å to 2.21 Å, but the structure of the remainder of the cage remains largely unchanged. Very similar changes in the carbon/phosphorus cage architecture emerge from a comparison of the crystallographically characterised species **6** and **3**, which are related by formal addition of a Cl^+ ion. Protonation at the other phosphorus center in **6′**, P(2), gives a minimum that lies some 4 kcal mol^{-1} above **5′**, confirming P(1) as the more basic site.

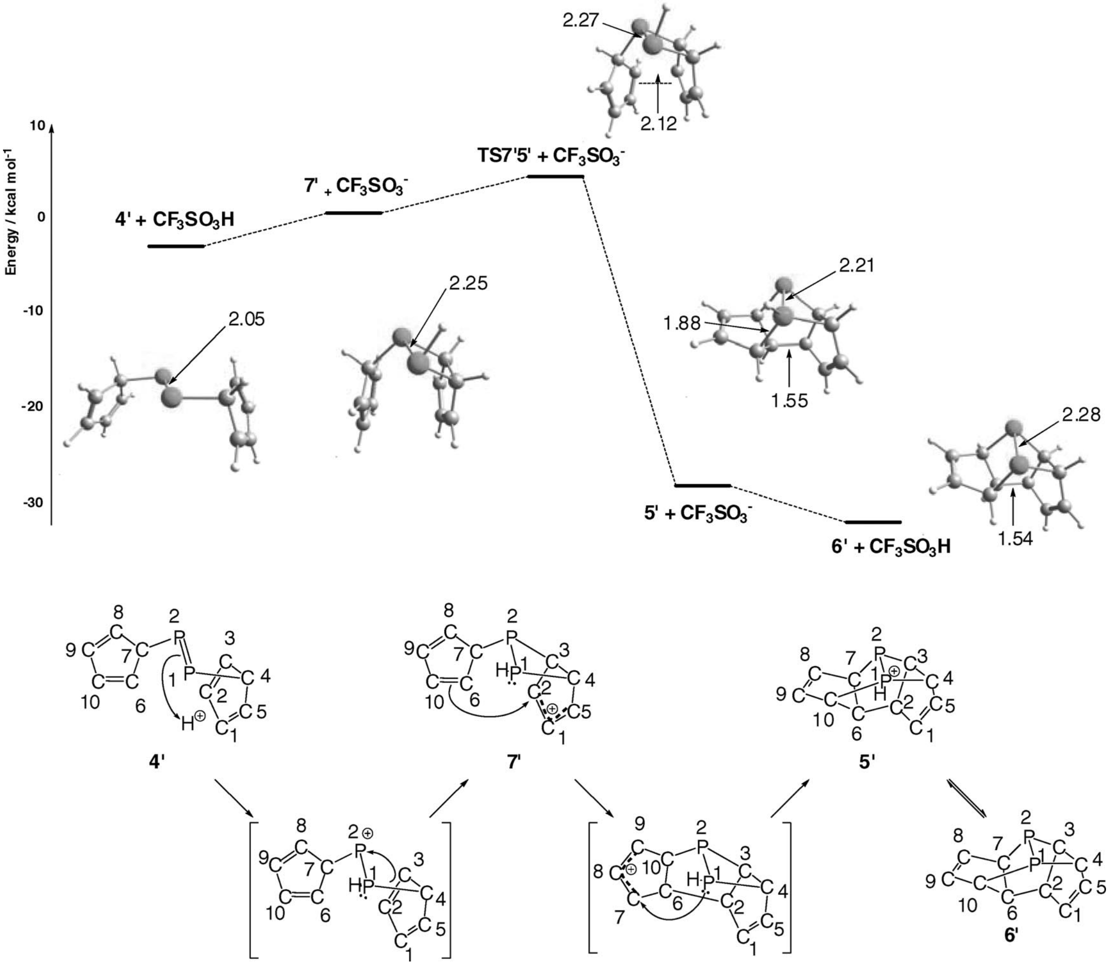


Figure 2. Potential energy surface for the cascade reaction connecting **4′** to **5′**. In the schematic diagrams shown in the bottom half of the figure, the transformations **4′** → **7′** and **7′** → **5′** are broken down into separate steps for clarity, although computationally we find both to be concerted; in addition, CH hydrogen atoms have been omitted for clarity in this part of the figure.

Turning to the overall thermodynamics of the reaction, the cage compound **6′** is 28 kcal mol^{-1} more stable than its P=P double-bonded diphosphene precursor **4′**, indicating that the stability of Jutzi's compound, **4**, in the absence of acid must have kinetic rather than thermodynamic origins. Inclusion of the methyl groups on the five-membered rings reduces the energetic separation (**4** → **6**) to only 5 kcal mol^{-1}, reflecting the greater steric crowding in the cage compound, but the conclusion that the latter is the thermodynamic product remains secure. The energetics of the protonation (**4′** → **7′**) and deprotonation (**5′** → **6′**) steps are referenced to the corresponding reaction of CF_3SO_3H: thus, the reaction **4′** + CF_3SO_3H → **7′** + $CF_3SO_3^-$ is calculated to be endothermic by 4 kcal mol^{-1}, whereas the deprotonation of **5′** is exothermic by the same amount. On this basis, we conclude that, in the presence of triflic acid, protonation/deprotonation will be facile, and in the remainder of the discussion we focus on the course of the reaction *after* the initial protonation step. The most striking observation is that protonation of **4′** at one of the two equivalent phosphorus centers does *not* yield the stable phosphenium cation intermediate shown in square brackets in Figure 2; instead, facile nucleophilic attack by the $C^2{=}C^3$ double bond on the developing cationic phosphorus center leads to intermediate **7′** where the four-membered P_2C_2 ring of **5′** is already formed and the positive charge is delocalized over the allylic unit C^2–C^1–C^5. Critically, then, once protonation occurs, formation of a P–C bond is barrierless. The second step (**7′** → **5′**) then involves nucleophilic attack of a $C^6{=}C^7$ double bond from the other five-membered ring on the allylic cation, leading to formation of both the C^6–C^2 and P^1–C^7 bonds (in Figure 2, the hypothetical structure that would result from formation of only the C^6–C^2 bond is shown in square brackets, but only **7′** and **5′** correspond to stationary points on the potential energy surface). The barrier to this reaction is very low (3 kcal mol^{-1}, **TS5′7′**) because a simple rotation about the P^2–C^{10} bond is all that is required to bring the two five-membered rings into an almost parallel conformation, where the π-systems can overlap and so form the C^6–C^2 bond.

The importance of H^+ in accelerating the cage-forming reaction is illustrated very clearly by the stability of the diphosphene **4** under aprotic conditions, despite the steep thermodynamic gradient leading to the cluster compound

6. An assessment of the potential energy surface in the absence of protons reveals a more complex mechanism involving electrophilic, rather than nucleophilic, attack by one of the C_5 rings on the P=P double bond leading to a zwitterionic intermediate. This substantial charge separation imposes a much larger barrier to isomerisation (32 kcal mol^{-1}), effectively retarding the process.

In summary, protonation of one of the phosphorus centers of the diphosphene **4** triggers a remarkable cascade reaction leading to the $C_{10}P_2$ cage, the key feature being the proximity of a C=C π-system to a developing positive charge on one of the phosphorus centers.

Experimental Section

General: All experimental procedures were performed under N_2 by using standard Schlenk line and glovebox techniques.

5: Trifluoromethanesulfonic acid, $HOSO_2CF_3$ (0.013 mL, 0.15 mmol) was added dropwise to a solution of $C_5Me_5P{=}PC_5Me_5$ (**4**, 0.05 g, 0.15 mmol) in dichloromethane (4 mL) at 0 °C. The intense yellow color of the starting material immediately dissipated to yield a yellow/brown solution. Compound **5** was produced quantitatively according to ^{31}P NMR spectroscopy. ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 25 °C): δ = 24.0 (d, J_{PP} = 178.6 Hz), 14.6 (d, J_{PP} = 178.6 Hz) ppm. ^{31}P NMR (162.0 MHz, dichloromethane, 25 °C): δ = 24.0 (dd, J_{PP} = 179, $^1J_{PH}$ = 425 Hz), 14.6 (dd, J_{PP} = 179, $^2J_{PH}$ = 15 Hz) ppm.

6: $SiHCl_3$ (0.51 mL, 5 mmol) was added dropwise to a solution of $[C_{10}Me_{10}P_2Cl][InCl_4]$ (**3**, 5 mmol, 0.5 M in CH_2Cl_2) at room temperature. This was followed by the addition of NEt_3 (0.70 mL, 5 mmol), also dropwise and at room temperature. This caused an immediate color change from deep red to yellow. The solvent was removed in vacuo and the product extracted into *n*-hexane (20 mL). The resulting pale yellow solution was filtered (porosity 3 sinter with Celite), reduced in volume and left to crystallise at –18 °C. **6** was produced quantitatively according to ^{31}P NMR spectroscopy and was isolable in a 55% crystalline yield. M.p. 138–142 °C (to form a yellow oil). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 25 °C): δ = 15.9, (d, J_{PP} = 148 Hz), 13.3 (d, J_{PP} = 148 Hz) ppm. EI-MS: *m*/*z* = 332 [M$^+$]. $C_{20}H_{30}P_2$ (332): calcd. C 72.27, H 9.10; found C 72.47, H 9.09.

Single-Crystal X-ray Diffraction Data for 6: $C_{20}H_{30}P_2$, M_r = 332.38 g mol^{-1}, crystal dimensions 0.2 × 0.1 × 0.05 mm, monoclinic, space group *P*2(1)/*n*, a = 7.958(2) Å, b = 16.827(3) Å, c = 13.471(3) Å, β = 92.55(3)°, V = 1802.1(6) Å^3, Z = 4, $\rho_{calcd.}$ 1.225 Mg/m^3, μ = 0.237 mm^{-1}, θ = 1.94–27.48°, measured reflections 20248, independent reflections 4133, R_{int} = 0.0780, R_1 ($I > 2\sigma$) = 0.1323, wR_2 (all data) = 0.2936. Diffraction data were collected at 100(2) K with a Bruker SMART APEX CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least squares using the SHELX suite of programs.[14] All non-hydrogen atoms were refined anisotropically. Despite repeated attempts, only poor-quality crystals were available, and hence the data set is relatively weak. CCDC-691307 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methodology: Full geometry optimizations were performed with the B3LYP functional[15] using 6-31G* basis sets on all atoms.[16] Transition states were located with the STQN algorithm[17] and all stationary points were characterized as minima or first order saddle points by their harmonic vibrational frequencies. All calculations were carried out with the Gaussian03 series of programs.[18] Total energies include solvation contributions (CH_2Cl_2 solvent) computed with the PCM approach at the gas-phase optimised structures.[19]

Supporting Information (see footnote on the first page of this article): Energies and cartesian coordinates for all stationary points reported in Figure 2.

Acknowledgments

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[10] The same ^{31}P NMR spectrum is observed when using a solution of HBF_4 in diethyl ether as the reagent, but no reaction is observed when using HCl in diethyl ether. Attempts to use other electrophiles, e.g. by reaction of **4** with MeOTf, resulted in a multitude of products whose identity we have not been able to discern.

[11] This reaction must proceed by broadside attack at the cationic phosphorus center.

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